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# Effect of Water on Hydrogen Permeability

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## EFFECT OF WATER ON HYDROGEN PERMEABILITY

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### SUMMARY

Doping of hydrogen with CO or CO<sub>2</sub> was developed to reduce hydrogen permeation in Stirling engines by forming low permeability oxide coatings in the heater tubes. An end product of this process is water - which can condense in the cold parts of the engine system. If the water vapor is reduced to a low enough level, the hydrogen can reduce the oxide coating resulting in increased permeability. This work was done to define the equilibrium level of water (oxygen-bearing gas) required to avoid reduction of the oxide coating. Results at 720 °C and 13.8 MPa have shown that, (a) pure hydrogen will reduce the coating, (b) 500 ppm CO (500 ppm water equivalent) does not prevent the reduction, and (c) 500 ppm CO<sub>2</sub> (1000 ppm water) appears to be close to the equilibrium level. Further tests will be made to define the equilibrium level more precisely and to extend the data to 820 °C and 3.4, 6.9, and 13.8 MPa.

### INTRODUCTION

Work has been done on high temperature alloys by NASA and its Contractors as part of the U.S. Department of Energy Stirling engine development program. One aspect of this work has been to investigate the phenomenon of hydrogen permeability and to develop techniques for reducing it to an acceptable level for Stirling engine operation.

Hydrogen permeation in a Stirling engine occurs in the heater head which may range in temperature from 700 to 900 °C. Hydrogen permeation is the phenomenon of the hydrogen working fluid diffusing through the heater head material. This loss of hydrogen by permeation through the heater head is only one of the major leak paths, the others being leakage at static and dynamic seals. All these must be minimized if the Stirling engine is to contain its hydrogen working fluid. Failure to contain the hydrogen will mean that the engine will suffer from loss of power and will need to be "recharged" frequently.

A method called doping was developed at NASA Lewis Research Center that can reduce permeability of the metal heater head tubes by an order of magnitude or more. This method consists of adding oxygen bearing gases to the hydrogen which form an impermeable oxide layer on the inside of the heater head tubes (ref. 1).

During later engine testing it was noticed that water had condensed in the area of the engine cooler. This condensation showed that the Stirling engine was capable of removing oxygen from the working fluid in the form of water. This removal of oxygen implies the possibility of removing the oxide from the

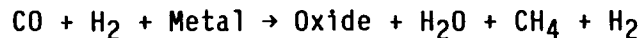
inside of the heater head tubes the oxide which is necessary to keep permeation at acceptable low levels.

#### METHOD OF DOPING

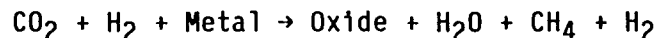
The Stirling material development program showed that metals were very permeable to hydrogen in the operational temperature range, with permeabilities of  $7 \times 10^{-6}$  to  $19 \times 10^{-6}$   $\text{cm}^2/\text{sec MPa}^{1/2}$ . This showed the need to develop a method to reduce permeability.

Testing showed that doping the hydrogen with small amounts of CO or CO<sub>2</sub> would reduce hydrogen permeability by an order of magnitude or more. Concentration of one-half to 1 percent proved effective. Other dopants such as ammonia, various hydrocarbons, and water (less than 100 ppm) were significantly less effective (ref. 1).

The CO and CO<sub>2</sub> reduced permeability of metals by forming an oxide on the inside of the sample heater head material. The overall reaction for forming this oxide is given below.



or



It is believed that the water that is formed from the CO or CO<sub>2</sub> plays an important role in forming and maintaining the oxide because it, like the CO and CO<sub>2</sub>, is an oxygen bearing gas. This reaction is shown below.



The oxide that was formed was a thin spinel and had thickness of one to three microns. Even though this oxide is very thin it can greatly reduce permeability because its permeability is four to five orders of magnitude lower than the base metal.

Figure 1 shows the effect that doping with 1 percent CO<sub>2</sub> has on CG-27. The first permeability measured after the first 5 hr run with 1 percent CO<sub>2</sub> was  $2.18 \text{ cm}^2/\text{sec MPa}$ . Permeability at the very beginning was much higher, perhaps in the range of  $8 \times 10^{-6}$  to  $12 \times 10^{-6}$   $\text{cm}^2/\text{sec MPa}$ . A significant amount of oxidation did occur during the first 5 hr test cycle. The permeability was then lowered to  $0.49 \times 10^{-6}$   $\text{cm}^2/\text{sec MPa}^{1/2}$  after 100 hr of running with 1 percent CO<sub>2</sub>.

Figure 2 shows the test rig that was used by NASA Lewis Research Center in its investigation of permeation. It is an oil fired furnace designed to provide the high temperature and simulate the combustion environment of an engine. Twelve modules as shown in figure 3 can be tested at one time. Each module consists of four u-shaped tubes, a manifold block, and a pressure transducer. A permeability coefficient for the material may be calculated from the pressure decline and from the geometry of the test module.

It should be pointed out that this is a static rig, that simulates only the heater head region of an engine. It does not simulate any of the flows to or from the cold side of the engine. It is because of this lack of simulation of other areas of an engine that the effect of water on hydrogen permeability was not readily observed during the original permeability research (refs. 1 to 4).

### Problem With Doping

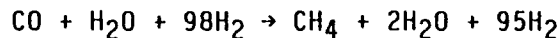
The problem with doping is that the CO or CO<sub>2</sub> dopant breaks down to form water and methane, and water is condensable. Figure 4 shows experimental and theoretical results for the breakdown of 1 percent CO<sub>2</sub> in high temperature hydrogen. The theoretical results are shown by the solid and dotted lines, the solid showing the formation of water and the separation of the last oxygen attached to a carbon. These theoretical results show that the breakdown of CO<sub>2</sub> is a two step process. The first step is the reaction of CO<sub>2</sub> and hydrogen to form methane and water. This first step is very fast, being well under way in 17 min. The second step is the breakdown of the CO into methane and water. Theoretical kinetics show that this final step should be very slow, starting to occur after five months.

#### Breakdown of CO<sub>2</sub> in hydrogen

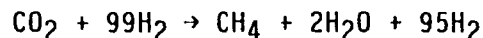
Step 1:



Step 2:



Overall reaction:



Experimental results from the rig and engine tests indicate that step two, of the two step breakdown of CO<sub>2</sub>, is very rapid. These points are also shown on figure 4. These test points show high levels of methane, which would not occur unless the breakdown of CO occurs much more rapidly than predicted.

Figure 5 shows the water saturation that would be determined by the temperature of various parts of the engine. The saturation concentration in the engine as determined by the engine cooler would be between 1000 ppm and 10 000 ppm, depending on operating conditions. The concentration, as determined by the hydrogen storage bottle temperature is generally below 300 ppm and could go as low as 10 ppm on a very cold day. A total oxygen content as determined by 10 ppm corresponds to a high purity hydrogen, which is known to cause high permeation.

The breakdown of the CO or CO<sub>2</sub> dopant into water and the condensation of this water means the engine will remove the oxygen originally invested in the dopant as condensate. After this oxygen based dopant is removed, the resulting dry, oxygen free hydrogen can then strip the oxide from the heater head until the heater head is in an unoxidized high permeability state.

This phenomenon of removing an oxide from heater head material is shown in figures 6 and 7. Figure 6 (ref. 4) shows pressure loss curves for a test module made from Inco 800 tubes that were oxidized in air. After oxidizing with air the module was filled and tested many times with high purity hydrogen. The lines show pressure versus time for the first, fourth, and seventh tests. It should be noted that this testing was done by refilling with high purity hydrogen after venting the residual hydrogen after each test.

Different results would be expected if the test module were refilled with high purity hydrogen without venting. This is because the water that would be formed by the reaction of the metal oxide and hydrogen would be left in. Calculations of the amount of oxygen invested in this oxide layer showed that several thousand ppm of water could be generated, which should be more than enough to maintain an equilibrium between the oxide and the water. Figure 7 shows the results of this testing. The top line shows the pressure for fully oxidized CG-27 and 1 percent  $\text{CO}_2$ . Two runs were then made with dry hydrogen, venting, and refilling each time. A greater rate of pressure decay was noted after these runs. Four runs were then made without venting. Although the hydrogen was originally dry, water was generated by the reduction of the oxide surface. Little or no change in rate of pressure decay was noted as a result of these four runs. Apparently enough water (oxygen-bearing gas) was generated by the initial oxide reduction to produce an equilibrium between reduction and oxidation of the metal oxide.

The increase in pressure decay when exposed to high pressure hydrogen indicates removal of the oxide. This removal of the oxide by high purity hydrogen is further supported by the detection of water after the first and last run with high purity hydrogen. This water was formed by the reduction of the metal oxide by hydrogen.

#### EQUILIBRIUM LEVEL TESTING

Testing has been done with hydrogen with dopant levels other than 1 percent in order to define the level of oxygen or water required to maintain equilibrium in the metal oxide - hydrogen - oxygen system and maintain a constant oxide and permeability level. Figure 8 shows permeability versus time for CG-27 that was observed by J. Misensik (ref. 3). The left side of the figure shows the decline in permeability from oxidizing with 1 percent  $\text{CO}_2$ . The right side shows the effect on permeability if continuing this test with 500 ppm  $\text{CO}_2$  (1000 ppm water) and 500 ppm CO (500 ppm water). The CG-27 exposed to 500 ppm CO shows a definite increase in permeability. The CG-27 exposed to 500 ppm  $\text{CO}_2$  showed little or no increase in permeability. These results indicate that the minimum water content to maintain minimum permeability is above 500 ppm and perhaps above 1000 ppm. These results also show that low total oxygen contents in hydrogen are consistent with increases in permeability.

More recent testing with 500 ppm  $\text{CO}_2$  show slightly different results as shown in figure 9. The left side of the chart shows permeability of CG-27 with 1 percent  $\text{CO}_2$  and the right side permeability with 500 ppm  $\text{CO}_2$ . The solid line shows the average of the two modules tested and the dotted lines the two individual modules. As may be seen one module maintained low permeability, while the other showed an increase. The reason for this is not fully understood, but is consistent with 1000 ppm being just below what is necessary to maintain minimum permeability.

## Future Testing

Because of this problem of low water contents causing high permeation, future testing will be done to define the minimum water content that is needed. This testing will look at pressures of 3.4, 6.9, and 13.8 MPa to simulate the engine operating region, and water contents between 200 and 2000 ppm where the critical range is expected to be. Further investigations will be done at 820 °C to include the new higher operating temperatures that are expected in the Mod I and future engines.

## CONCLUDING REMARKS

Testing to date has shown that 1000 ppm water, as determined by 500 ppm CO<sub>2</sub> is very near the minimum that is needed to maintain low permeability. These conditions indicate a minimum dew point in the engine of 54 °C. Lower temperatures may result in depletion of needed oxygen-bearing gas and reduction of the permeation-resistant oxide.

Testing with 500 ppm water, as determined by 500 ppm CO has shown an apparent increase in permeability.

Testing with high purity hydrogen has shown increases in permeability and water in the hydrogen at the end of the test. Both of these observations indicate that the oxide on the inside of the tubes can be removed by dry hydrogen. This testing also showed that the water that was generated from stripping the oxide would stabilize permeability, indicating that an equilibrium between the oxide and the water in the hydrogen could be obtained.

The removal of the inside oxide to form water, combined with the Stirling engine's ability to remove water by condensation in its low temperature areas, provides a mechanism that can remove all the oxide from the inside of the heater head which would result in high hydrogen permeation loss rates.

Testing will continue to define precisely the required water level to maintain oxide equilibrium and the desired low permeability.

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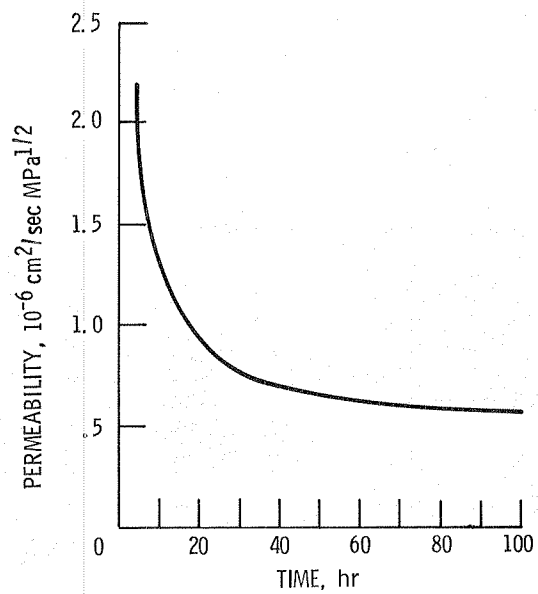


Figure 1. - Permeability versus time for CG-27 (1% CO<sub>2</sub> BAL H<sub>2</sub>)

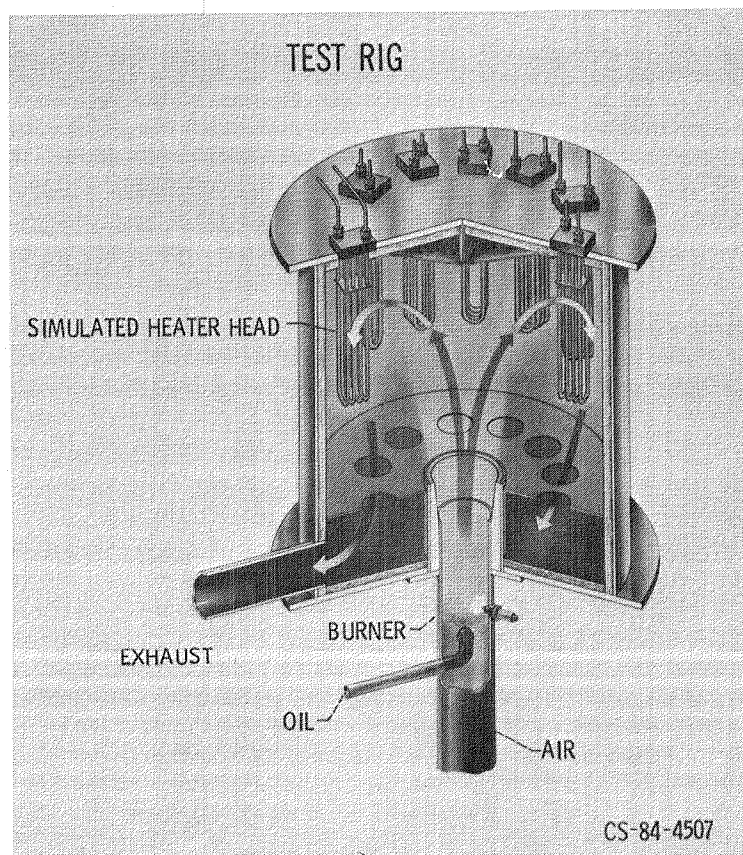


Figure 2. - Test rig.

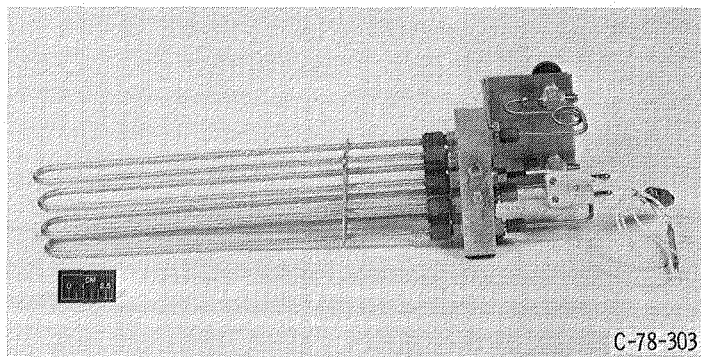


Figure 3. - Test module.

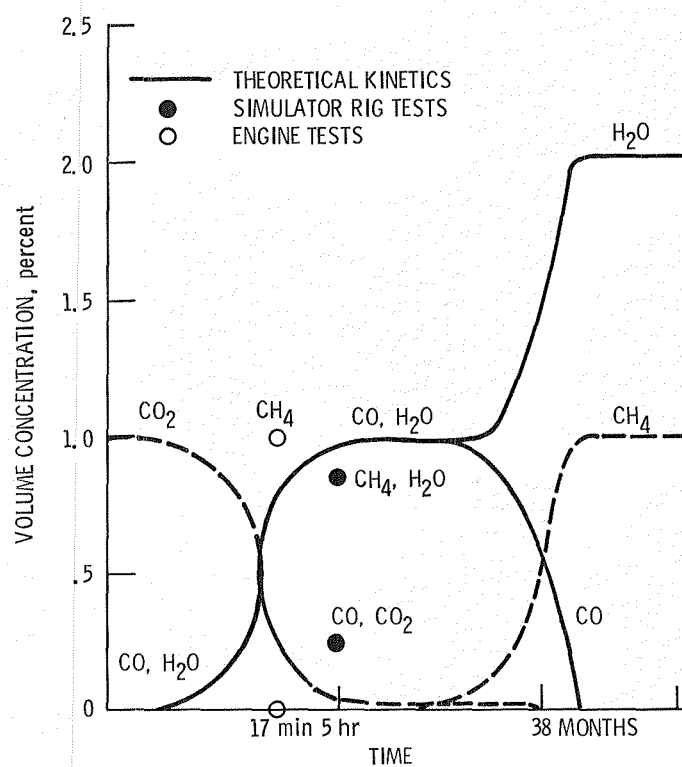


Figure 4. - Doped hydrogen kinetics pressure, 10.5 MPa; temperature, 730 °C; 1%  $\text{CO}_2$ , BAL  $\text{H}_2$ .

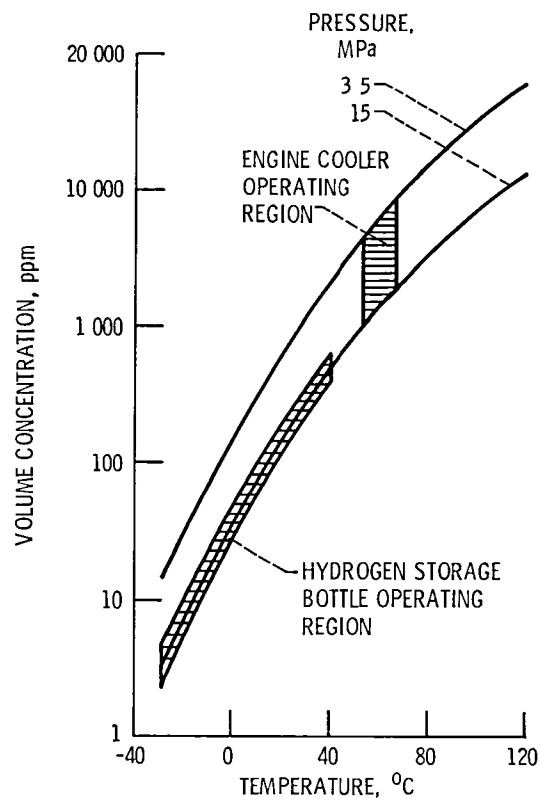


Figure 5. - Saturation concentration of water.

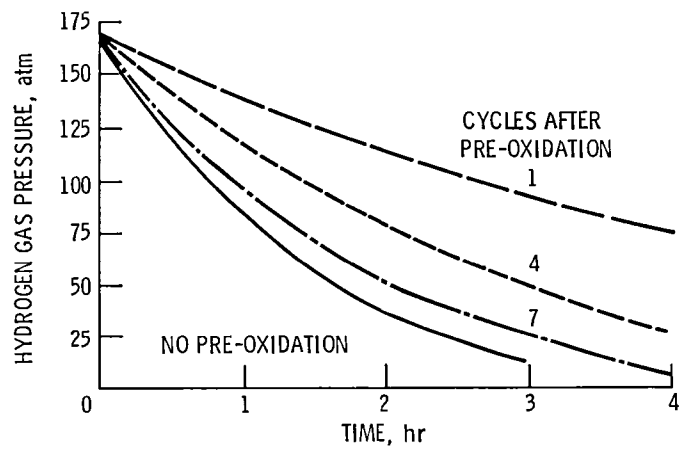


Figure 6 - Hydrogen loss through oxidized Incoloy 800 tube wall at 760 °C.

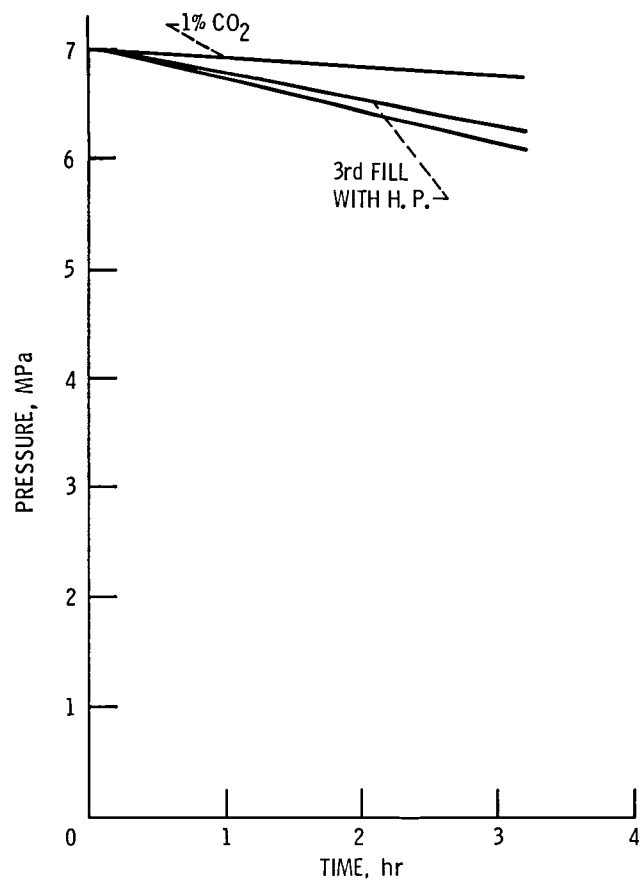


Figure 7. - Pressure decay for CG-27 temperature, 760 °C.

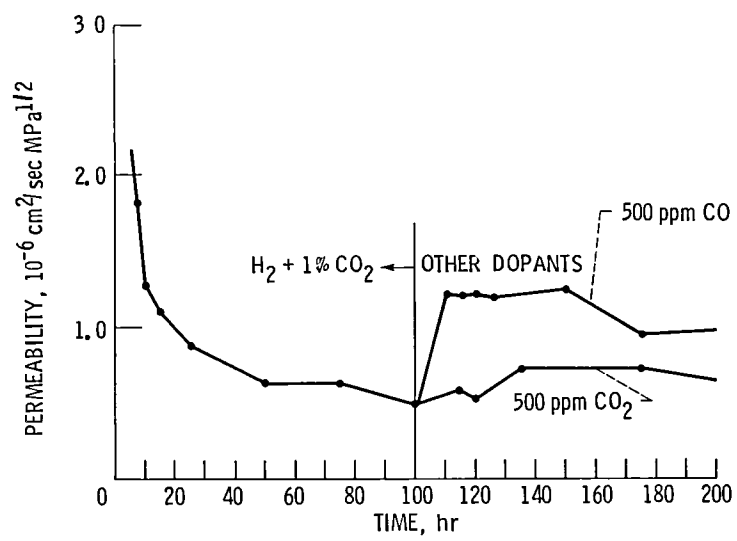


Figure 8 - Permeability versus time for different dopants.

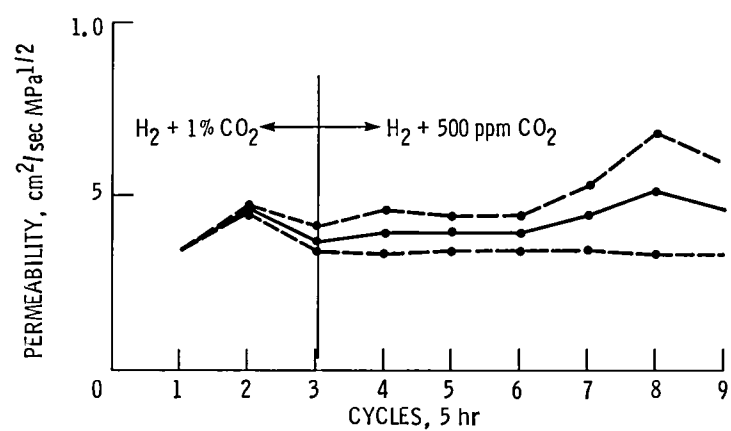


Figure 9. - Hydrogen permeability of CG-27 with 1000 ppm total oxygen.

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